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HYDROCHEMISTRY OF HUB DAM OF PAKISTAN: WEATHERING PROCESSES AND WATER QUALITY ASSESSMENT

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ABSTRACT

Water samples were collected from four sites of Hub reservoir and has been analyzed for assessing the ionic chemistry, weathering and geochemical processes that control the quality of water. Calcium, sodium and bicarbonate are found as the dominant chemical characteristic of the Hub reservoir. It is inferred that weathering of rock in the catchments area is mainly responsible for composition of water chemistry. The order in cations abundance is $Ca^{2+} > Na^{+} > Mg^{2+} > K^{2+}$, contributing on average (mg l^{-1}) 8.43, 8.39, 2.16 and 0.87 % respectively. The water composition revealed that the rock weathering is the controlling factor at all sampling sites. Plots of saturation index of calcite (SIc) vs saturation index of dolomite (Sid) indicated the under saturation. The recorded values of sodium adsorption ratio (SAR), percent sodium (%Na), and residual sodium carbonate (RSC) showed that water of Hub reservoir is excellent to good quality regarding irrigation purpose The obtained results are under the permissible limit of WHO standard indicating the suitability of water for the different purpose.

KEYWORDS: Hydrochemistry, Hub Reservoir, Water Quality Assessment

INTRODUCTION

Composition of Hub reservoir is derived from the inflow river system; weathering and geochemical process is operated in the catchments. The main chemical processes, which releases ions into solutions are hydrolysis, reduction, oxidation or chelation (Drever 1988). Wetlands are one of the most productive ecosystems, comparable to tropical evergreen forests in the biosphere and play a significant role in the ecological sustainability of a region (Khan and Ghalib, 2006). This (water) is nature‘s most wonderful, abundant and useful compound and it is the basis of all lives-ecological resources for the flora and fauna of our earth and a fundamental necessity for all lives. Without a proper functioning water supply, it is difficult to imagine productive human activity, be agriculture or forestry, livestock, farming or fisheries, trade or industry (Tatawat et al. 2007). Natural composition of reservoir waters are essential regulated by the breakdown of rock matrix in response to the reactive rain water containing dissolved carbon-dioxide however deviations in natural water chemistry could be introduced by man at any stage (Singh et al. 2005).

Hub dam (25° 15‘N, 67° 07´E) constructed across Hub River in 1981, at a distance of 56 km North of Karachi falls in the provinces of Sindh and Balochistan (Figure1). Main Dam is 15,640 m long of which 5,400 m lies in Balochistan and 10,240 m in Sindh. It has been designated as a Ramsar Site in May 2001. Hub Dam has also been declared as a Wildlife Sanctuary in Sindh established in 1972 for the preservation of water birds and the fish Mahsheer.

Hub dam lies in the southern part of Pab Range. The geology of the area comprises mainly of Nari and Gaj formations of Oligocene and Miocene respectively. Gaj Formation consists of thick beds of clay with few limestones in the middle part. Gaj Formation is more resistant than the underlying Nari formation and the contact between Nari and Gaj formations are comfortable.

Hub Dam is important water source for Karachi hence its need special attention. Thus the objective of the present study was to assess the seasonal variations in the physico-chemical parameters of Hub Dam and a detail study of its hydro geochemical study at its four sampling sites. The study has been carried out to determine the major ion chemistry of Hub Dam and the water quality assessment for its suitability for domestic and irrigation purpose.

MATERIALS AND METHODS

For the study of physicochemical parameters four different sampling sites during 2011-2012 viz. Main Dam (N 25º 14´ 35.5, E 67º 06´ 45.8), Hub Canal (N 25º 14´ 26.6, E 67º 06´ 48.6), Spill way (N 25° 17´ 23.2, E 67° 05´ 55.6) and shallow water (N 25º 14´ 55.3, E 67º 08´ 56.3) were selected. Samples were collected in 1000 ml polyethylene bottles, which were cleaned sequentially, tap water rinse, 24 hour soak in 1% HNO_3 and several distilled water rinse. The bottles were dried at 100 ºC for an hour, cooled at room temperature, capped and labeled. After collecting the samples, 10 ml HNO_3 was added to the samples (Gorsuch, 1976; Santa et al., 1986).

The pH was recorded with Orion 420 pH meter. Alkalinity was measured by titration method with 0.02 M hydrochloric acid (Electrometric method No.15 WHO, 1982).

Conductivity was measured by light and dark bottles method (Welch, 1952). By gravimetric methods, sulphate and TDS were determined; chloride by argentometric method, calcium, magnesium, and hardness were recorded by the help of EDTA titration procedure, sodium and potassium were measured by flame photometer. Bicarbonate, salinity and colour were measured by using standard method APHA (1998). Parameters such as the sodium adsorption ratio (SAR), percent sodium (%Na), and residual sodium carbonate (RSC) were also estimated mathematically.

RESULTS AND DISCUSSIONS

- **Hydrochemistry**

During the present study the collective mean of all parameters at all sampling sites are collected in summer, monsoon and winter period are shown in Table 1. The composite pH of all samples sites in all seasons was noted 7.05, indicating near neutral pH. The measured pH in different seasons is slightly fluctuated from 6.88 to 7.24. The seasonal variation in the TDS and HCO_3 ions in the water are mainly responsible for variations in pH values. The mean value of electrical conductivity of collected samples are 563, 529 and 566 µS/cm for summer, monsoon and in winter respectively (Table.1). The recorded values of all sampling sites as the collective mean value of TDS are 539.75 mg l^{-1}, 496.94 mg l^{-1} and 498.44 mg l^{-1} for summer, monsoon and in winter respectively. High TDS was noted in summer due to excessive evaporation.

This study signifies Ca > Na > Mg > K abundance trend in the major cations. Anions exhibit HCO_3 > Cl > SO_4 order of distribution in the Hub Dam reservoir water. Bicarbonate ions accounts for 23%, 23% and 25% in summer, monsoon and winter seasons correspondingly. The observed mean values of all sampling sites of HCO_3 ions are 151.88, 139.88 and 155.88 mg l^{-1} in summer, monsoon and winter. Sulphate accounts for 14% in summer, 14% in monsoon and 18% in winter of the total anions. The average value of SO_4 in all selected sites are 73.81 mg l^{-1}, 71.38 mg l^{-1} and 73.13 mg l^{-1} for summer, monsoon and in winter respectively. Concentration of chloride varies in different seasons and the collective mean values of Cl of all sampling sites are 96.63 mg l^{-1}, 92.81mg l^{-1} and 92.00 mg $l^{-1}$for summer, monsoon and in winter.

The collective mean value of Ca^{2+} in all selected sites is noted as 52.75 mg l^{-1}, 50.88 mg l^{-1} and 52.38 mg l^{-1} in summer, monsoon and in winter correspondingly. The concentration of Na was low in the all types of water and it ranges from 49.63 to 53.75mg l^{-1}. The collective mean value of Mg in all selected sites is 14.385 mg l^{-1}, 12.94 mg l^{-1} and 12.75 mg

l^{-1} were recorded during summer, monsoon and winter period. The contribution of K was below unity (0.8%) and shows minor variation in the K content in water of Hub Dam area. It is estimated 5.54, 5. 13 and 5.43 mg l^{-1} in all seasons (Table 1).

Calcium and HCO_3 ions exhibits comparable trend, indicating weathering of limestone as a dominant process. However, some clustering is observed in all types of samples in summer (Figure 2a). It is important to note that Na vs HCO_3 trend is nearly similar (Figure 2b). In majority of the cases, Na has good relation with Cl ions. The relation in the present study is not linear (Figure 2c). In natural water, Mg is commonly associated with SO_4 ions. The plots (Figure 2d) exhibit a linear trend, but the molar ratio of SO_4 is more. This can also be visualized from mutual relation of SO_4 and Ca and Na, both Ca and Na display good relations (Figure 2e & f). Probably the water of the study area have low amount of Mg, derived from the carbonate rocks. Relatively high SO_4 in the water is due to dissolution of gypsum, which is abundant in the rocks of Nari and Gaj formation of the study area.

- **Mechanism Controlling Water Chemistry**

Rock weathering, atmospheric precipitation and evaporation are the main processes, influencing the chemical composition of freshwater. The weathering of carbonate rocks contributes Ca^{2+}/HCO_3^- ions, Na^+/Cl^- from precipitation and Mg^{2+} and $SO4^{2-}$ from the weathering and oxidations of sulphate and sulphite ores. Total dissolved solids in the water are the product of these sources which may modified by the process of evaporation (Singh et al., 2005).

Gibbs (1970) diagrams summarized the above concepts and proposed descriptive model regarding the three processes. The diagrams consist of two separate figures in which TDS are plotted on ordinate, while Na^+/Na^++Ca^{2+} and Cl^-/Cl^-+HCO_3 are plotted on abscissa. The plots of Hub reservoir, collected in different seasons are occupied in the area of rock dominance, indicating that the water characteristics are mainly controlled by the rock weathering in all selected sampling sites (Figure 3a & b).

In the Hub reservoir, Ca^{2+} and Mg^{2+} together constitute 10.6% of the total cations and HCO_3 contribute about 23% to the total anionic balance. The concentration of Na in the analyzed waters is relatively higher than chloride and maximum Na/Cl (0.3-0.4) and (Na+K/Cl) 2.1 indicating that alkalis in the Hub reservoir attributed from some other source rather than precipitation. The evaporate encrustations of sodium/potassium salts developed in some few part of the drainage area due to cyclic wetting and drying during high and low flow period. This aids the formation of alkaline / saline soils, which may also serve as a source of Na and K (Sarin et al. 1989).

The $(Ca+Mg)/HCO_3$ ratio marks the upper limit of bicarbonate input from the weathering of carbonate rock (Stallard and Edmond 1983). The scattered diagrams (Figure 4) shows variation between $(Ca^{2+}+Mg^{2+})$ versus (HCO_3^-) and $(HCO_3^-+SO_4^{2-})$ on each sites of sampling. The excess of Ca+Mg over bicarbonate was found in almost all the sites revealed some extra source of Ca and Mg and requiring that sites of the excess cations has to be maintained by other anions like sulphate and chloride. However, the relation between Ca+Mg and HCO_3 at spill way is different. The water of spillway falls below the 1:1 in samples collected in winter seasons (Figure 4).

The excess of bicarbonate over Ca+Mg requires that part of the alkalinity should be balanced by alkalies (Na+K). Similarly, (Ca+Mg) vs (HCO_3+SO_4) diagram shows good correlation among the ions. One sample representing spillway plots below the 1:1 equiline, indicates high HCO3 and SO4 ions in the water. In contrast, water collected from main dam during different seasons are plotted above the 1:1 line (Figure 4). Probably the high amount of (HCO_3+SO_4) ions is balanced by the alkalis (Na+K).

Further, the plot of (Ca^{+2} + Mg^{+2}) versus Total Cations (TZ^{+}) shows that the most of the plotted points fall near at Hub canal below the equiline (Figure 4c). The departure is being announced the high concentration reflecting an excess contribution of Na and K with excess amount of dissolved solids. Cations fractions are derived from evaporated complexes with chloride are as to be insignificant for the hub reservoir since the reservoirs have usually high chloride concentration and Na/Cl ratio i.e. (0.41) at all sites. The water samples is characterized by high Mg/Na ratios i.e. (0.24–0.28) whereas input from evaporates will have very low (<0.2) Mg/Na ratios (Negrel and others 1993). The dissolved chemistry of reservoirs is likely to be estimated by the component mixing from carbonates and the significance source can be explained by cationic abundance and their ratios (Singh et al., 2005). Water draining only carbonates show Ca^{2+} and Mg^{2+} dominated reservoirs and Ca/Na ratios close to 50%, Mg/Na close to 10 and HCO_3/Na ratios close to 120 (Negrel and others 1993; Meybeck 1986; Stallard 1980).

The molar Ca/Na of average crustal continental rocks is close to 0.6 (Taylor and McLennan 1985). The chemical composition assigned for the silicate end member is Ca/Na=0.35±0.15, Mg/Na =0.24±0.12, HCO_3/Na=2±1 (Gaillardet et al. 1999). The observed mean molar ratios at all sampling sites viz. main dam, hub canal, spill way and shallow water in all seasons of Ca/Na (0.98), Mg/Na (0. 25) and HCO_3/Na (3. 14) in the hub reservoir water are much lower than those of the waters draining carbonate lithology. This indicates that the dissolved chemistry of the Hub reservoirs is essentially controlled by the component mixing of carbonates and estimated value at all sites is found higher from the described value for the silicate end member by Gaillardet et al. (1999).

The observed (Ca+Mg) / (Na+K) equivalent ratio of 2.6 in the analyzed waters suggests that the chemical composition of the reservoirs is under the influence of carbonate. Estimation of bicarbonate contribution from the weathering of carbonate weathering shows that on an average 63% of the HCO_3 is contributed by carbonate weathering in the studied reservoir. The equilibrium state of the water with respect to a mineral phase can be determined by calculating a saturation index (SI) using analytical data.

The plot of saturation index of calcite (SIc) versus saturation index of dolomite (SId) demonstrates that almost the water of all the sampling sites are undersaturated with respect to both calcite and dolomite in summer, monsoon and winter (Figure 5). The plots within the domain of undersaturation show variation in the saturation in different seasons. This suggests further dissolution of calcite and dolomite as a result more Ca and Mg ions can be concentrated in the water of Hub dam reservoir. The situation of saturation is probably the consequence of evaporation effects and low level of the water of this reservoir and favouring the precipitation of carbonates (Hardie and Eugster 1970).

- **Assessment of Water Quality**

The water quality yield information about the environments through which the water has circulated (Janardhana Raju, 2007). The quality of water of Hub reservoir for drinking and irrigation purposes is assessed by comparing the result with prescribed values of World Health Organization (WHO, 2004).

- **Water Quality for Human Consumption**

The World Health Organization (WHO, 2004) and the Environmental Quality Standard for drinking water (Ministry of Environmental Protection agency) details the criteria for the physicochemical parameters in drinking water. All the calculated values of hydrochemical parameters at all selected sites are compared with the prescribed values of WHO standard and NEQS (Pakistan) and the obtained results of all parameters of this reservoir indicates that the water of Hub dam is safe and suitable for the drinking supply, domestic use and irrigation purpose by comparing the permissible limit (Table 1).

- **Irrigation Water Quality**

Sodium adsorption ratio (SAR), percent sodium (%Na) and residual sodium carbonate (RSC) were calculated to check the Hub reservoir water for irrigation purpose. To assess the water suitability for irrigation purpose electrical conductivity and sodium concentration are very essential elements. The total concentration of soluble salts in irrigation water can be expressed for the purpose of classification of irrigation water as low (EC = <250µS cm^{-1}), medium (250– 750µS cm^{-1}), high (750–2,250µS cm^{-1}) and very high (2,250– 5,000µS cm^{-1}) salinity zone (Richards 1954). According to this scheme all water samples are medium in salinity (Table 2). A maximum salt concentration (high EC) and a high sodium concentration lead in water formation of saline soil, and to development of an alkaline soil respectively. The water for the irrigation purpose, the sodium or alkali hazard of water is estimated by the absolute and relative concentration of cations and is expressed in terms of SAR and it can be calculated by the given formula:

SAR = Na / √(Ca++Mg)/2 Where Na, Ca and Mg are in meq/l.

A significant relationship is existed between SAR values for irrigation and the extent to which sodium is absorbed by the soils. The water if used for the irrigation purpose having the low concentration of calcium and high concentration of sodium, the cation-exchange complex may become saturated with sodium and can damage the soil structure owing to dispersion of the clay particles. The estimated mean values of SAR in the study area were calculated at all selected sites ranges from 8.76 to 9.15 and electrical conductivity was also measured in ranges from 551.75 to 555.16 at all sampling sites. The estimated sodium percentage (%Na) in the Hub reservoir area is 46.69, 46.56 and 45.69 % in summer, monsoon and in winter. %Na is estimated by the following equation:

$\% Na = (Na^{+}) x100/(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})$ (values in meq/l)

A plot of analytical data on the Wilcox (1955) diagram relating electrical conductivity and sodium percent indicates that at the all sampling sites viz. main dam, hub canal, spill way and shallow water is excellent to good quality and may be used for irrigation purposes (Figure 6). RSC has been calculated to quantify the effects of carbonate and bicarbonate in the study areas. A high value of RSC in water value leads to an increase in the adsorption of sodium on soil (Eaton 1950). The RSC has been estimated by the following equation:

$RSC = (CO_3^{2-} + HCO^{-}_3) – (Ca^{2+} + Mg^{2+})$

The RSC value of all the selected sites of Hub reservoir varies between (181– 442 mg l^{-1}), is revealing that the water of this reservoir is suitable for the irrigation purpose. The evolution of water and relationship between rock types and water composition can be evaluated by the trilinear Piper diagram (Piper 1944). The piper diagram is a graphical representation of the chemistry of a water samples. The cations and anions are shown by separate ternary plots. The apexes of the cation plot are calcium, magnesium and sodium plus potassium cations. The apexes of the anion plot are sulfate, chloride and carbonate plus hydrogen carbonate anions. The two ternary plots are then projected as a diamond-shaped diagram that combines the composition of cations and anions. The diagram of chemical data on trilinear diagram indicates that a majority of the hub reservoir water falls in the areas of mixed ions type (Figure 7). The ionic composition of water represents no dominant type. The variations and distributions of hydrochemical facies of Hub reservoir at all sampling sites show that Ca-Mg-Cl is the dominant hydrochemical facies.

CONCLUSIONS

The present investigation indicates the reservoir water is near alkaline in nature. Calcium and sodium are the dominant cations and bicarbonate and sulphate are the dominant anions. The water chemistry is largely controlled by rock

weathering estimated from Gibbs diagram. High concentration of HCO_3 and (Ca+Mg) and ratios of Ca/Na, Mg/Na, HCO^-_3/Na^+ suggest combined influence of carbonate and silicate weathering in controlling the water chemistry of the studied reservoirs. Observed maximum ionic concentration of bicarbonate, chloride and sulphate at all selected sites in Hub reservoirs reveal the input from the weathering of sulphide minerals. The water chemistry shows undersaturation with respect to calcite and dolomite at all sampling sites. The estimated values of SAR, %Na and RSC indicates that water is excellent to good quality and may be used for irrigation purpose without any hazard. The diagram of chemical data on Piper diagram indicates that the majority of the hub reservoir water falls in the areas of mixed Ca-Mg-Cl. All the physicochemical parameters were recorded to be within the limits of WHO Standard. Therefore, the water of Hub Dam is chemically safe and fit for human consumption, irrigation and for the growth of aquatic flora and aquatic biodiversity.

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APPENDICES

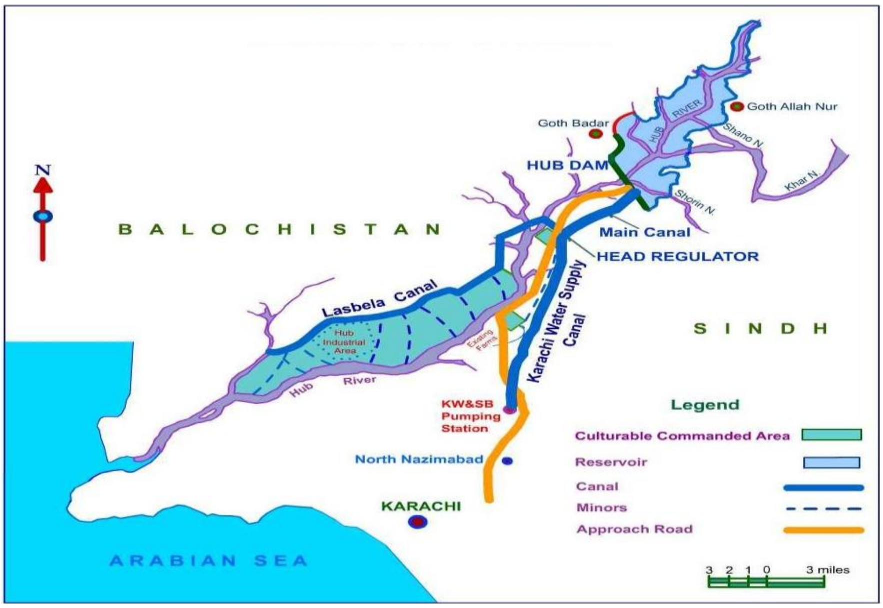

Figure 1: Map Showing the Water Supply at Hub Dam

Table 1: Collective Mean Value of all Sampling Sites During 2011- 2012

Parameters	2011			2012			WHO International Standards, 2004	NEQS Pakistan
	Summer	Monsoon	Winter	Summer	Monsoon	Winter		
ph	7.01	7.16	7.14	6.89	7.09	7.01	6.5 - 9.2	6.5-8.5
TDS (mg/l)	539.75	496.94	498.44	548.44	498.31	495.56	1000	<1000
Alkalinity (mg/l)	79.63	70.69	74.38	82.25	70.25	72.69	30 - 500	
Salinity (mg/l)	0.38	0.34	0.35	0.37	0.38	0.34	-	-
Conductivity (µs/cm)	563.19	529.31	566.06	568.56	513.19	551.56	1500	
Hardness (mg/l)	189.33	172.13	173.50	188.44	170.38	172.94	100 - 200	
Bicarbonate (mg/l)	151.88	139.88	155.88	163.94	121.19	123.94	240	
Sulphate (mg/l)	73.81	71.38	73.13	78.44	72.13	72.63	250	
Chloride (mg/l)	96.63	92.81	92.00	111.31	95.88	97.31	250	<250
Carbon Dioxide (mg/l)	1.40	1.41	1.43	1.32	1.43	1.49	-	-
Dissolved Oxygen (mg/l)	4.54	3.91	4.13	4.56	3.89	3.91	-	-
Calcium (mg/l)	52.75	50.88	52.38	56.56	50.69	53.81	200	
Magnesium (mg/l)	14.38	12.94	12.75	16.44	13.88	13.94	150	
Sodium (mg/l)	53.25	50.38	51.56	53.75	50.63	50.88	200	
Potassium (mg/l)	5.54	5.13	5.43	5.74	5.07	5.41	200	
Na %	46.69	46.56	45.69	45.61	46.14	44.86	-	-
SAR	9.19	8.92	9.04	9.04	8.85	8.61	-	-
RSC	273	248.18	264.25	280.58	224.16	237.33	-	-

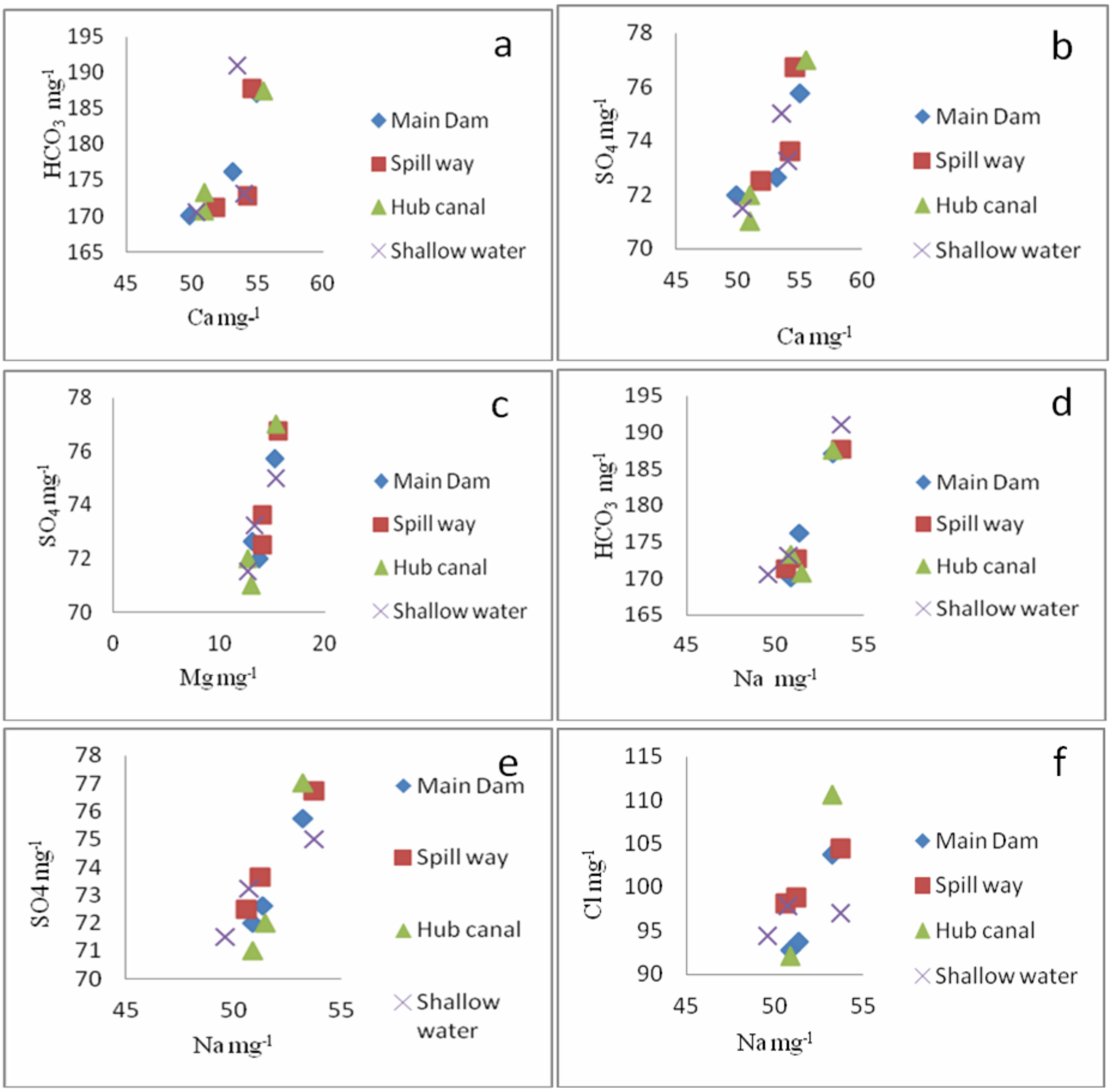

Figure 2: x-y Scattered Diagram between Different Parameters Viz. Ca versus HCO_3, Mg versus SO_4, Na versus Cl, K versus Cl, Ca versus SO_4, Ca versus Cl, Mg versus HCO_3, Mg versus Cl, Na versus HCO_3 and Na versus SO_4

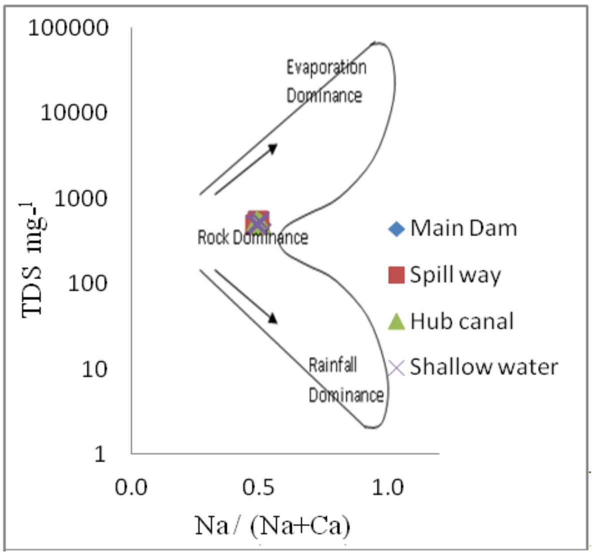

Figure 3a: Plot of Na/Na+Ca versus TDS at Main Dam

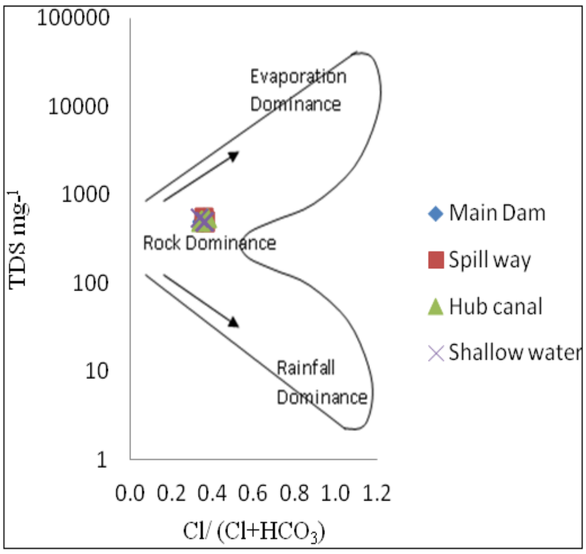

Figure 3b: Plot of Cl/Cl+HCO_3 versus TDS at Main Dam

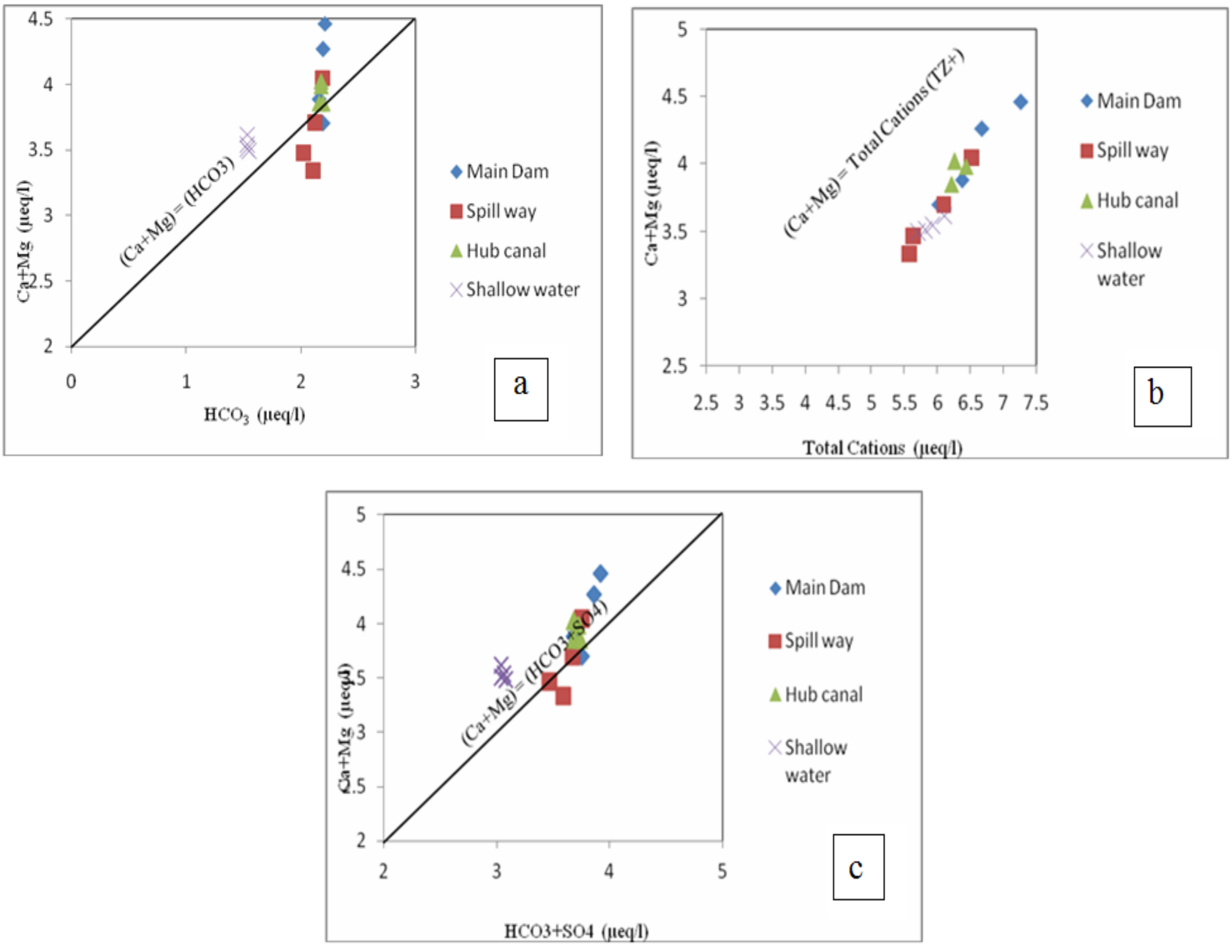

Figure 4: x-y Scattered Diagram between Different Parameters

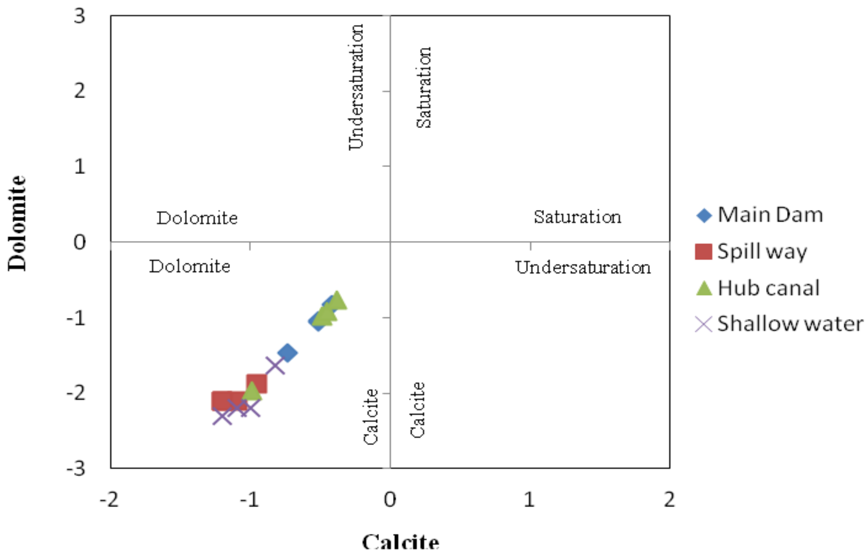

Figure 5: Saturation Indices for Calcite (SIc) and Dolomite

Table 2: Salinity and Alkali Hazard Classes after Richard (1954)

Quality of Water	Electrical Conductivity	Sodium Adsorption Ratio (Equivalent Per Mole)
Excellent	< 250	<10
Good	250-750	10-18
Doubtful	750-2250	18-26
Unsuitable	>2250	>26

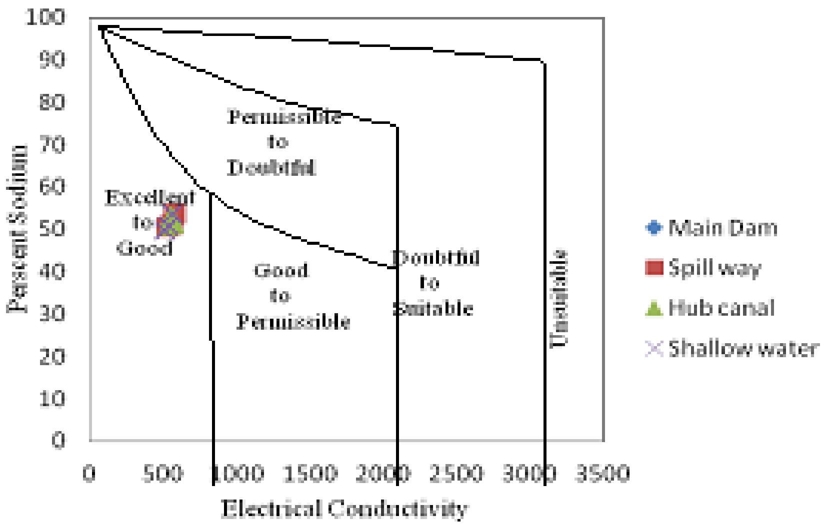

Figure 6: Plot of Sodium Percent vs Electrical Conductivity

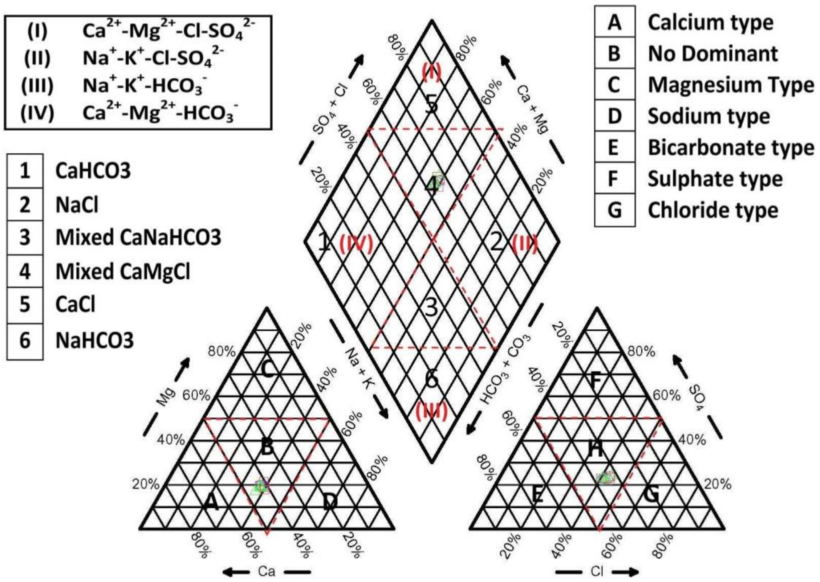

Figure 7: Piper Diagram Showing General Hydro Chemical Signature